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Discovery of Superglue Shows Power of Pursuing the Unexplained

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IRI ACHIEVEMENT AWARD ADDRESS

Discovery of Superglue Shows Power of Pursuing the Unexplained

Heading into the future is akin to a caterpillar entering a cocoon—the caterpillar doesn't know he will come out as a butterfly, all he knows is that he's alone, in the dark, and a little scared.

Harry W. Coover

OVERVIEW: *Cyanoacrylates are a unique chemical species that today is having a significant impact on a wide range of consumer and industrial applications, as well as promising to answer the surgeon's dream of a tissue adhesive and hemostatic agent for a wide range of surgical procedures. Its astonishing adhesive properties were discovered in 1951 when a ruined instrument in the research laboratories of the then Tennessee Eastman Company led to a flash of insight followed by inevitable years of innovation. The discovery serves as yet another reminder to be open-minded and curious enough to pursue unexplained results that may unlock new secrets and lead to future exciting discoveries.*

The discovery of cyanoacrylate adhesives—popularly known as Superglue—is a long-time favorite story of industrial researchers. For those who have not heard it (recounted, for example, in "A Day of Serendipity, a Decade of Hard Work," *Research Management,* Nov. 1980, pp. 37–40), I shall relate some of the highlights.

Serendipity, defined as a lucky accident, played a large part in the discovery of cyanoacrylate adhesives, but only when my mind was finally ready to see that the accident was really a bit of luck.

As a young chemist at the bench during World War II, I was assigned the problem of finding an optically clear plastic from which precision gunsights could be cast. I was working with some cyanoacrylate monomers which showed promise, but I was plagued by a recurring problem: Everything these monomers touched stuck to everything else, which I recorded. However, I didn't see this as serendipity, just as a severe pain! I was thinking gunsights, and nothing but gunsights. The adhesive qualities of these monomers were a serious obstacle in my path—certainly not a lucky accident.

The research was successful, but the end of the War brought this project to an end. I forgot the stubbornly-sticking cyanoacrylates. Serendipity had knocked, but *I didn't hear it.*

A Ruined Instrument

Moving ahead a few years to 1951, there was a need to discover stronger, tougher and more heat-resistant acrylate polymers for jet plane canopies. I was now supervising a new crop of eager young chemists who were investigating the properties of the same cyanoacrylate polymers that I had been working with earlier.

The monomers were difficult to make, even more difficult to purify and still more difficult to analyze for purity. One of my group, Fred Joyner, prepared what he thought was a pure sample of ethyl cyanoacrylate and decided to measure its refractive index in order to characterize its purity. The measurement was made and recorded.

When Fred attempted to separate the prisms, he could not! He took his problem to his laboratory supervisor, Newt Shearer, but nothing they could think of would free the prisms. Finally, Fred and Newt came to me to report that they had ruined a $700 instrument. (That may not sound like much today, but it was real money then.) Any concern I had about the refractometer was swept away by the sudden realization that what we had was not a useless instrument but a unique adhesive. *Serendipity* had given me a second chance, but this time the mental process led to inspiration.

Immediately, I asked Fred for a sample of his monomer and began gluing everything I could lay my hands on—glass plates, rubber stoppers, metal spatulas, wood, paper, plastic—in all combinations. Everything stuck to everything, almost instantly, and with bonds I could not break apart. In that one afternoon, cyanoacrylate adhesives were conceived, purely as the result of serendipity.

One cannot help wondering how many potentially important inventions lie dormant in the recorded

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Harry Coover received the 1999 Industrial Research Institute Achievement Award for the discovery and innovation of cyanoacrylate adhesives. His article is adapted from the address he delivered upon accepting the Award at the IRI Fall Meeting in San Antonio, Texas, Oct. 1999.

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observations of scientists which at the time were judged to be irrevelant to their research objective. This should serve as a reminder to all of us to be open-minded and curious enough to pursue unexplained events and unexpected results that may unlock new secrets and lead to new and exciting discoveries in the future.

The important story today, however, is the broad spectrum of unique and valuable applications of cyanoacrylates developed over the past 40 years.

Amazing the TV Audience

To make known to a broad audience the unique and fascinating properties of the new instant adhesives so that useful applications could be found, I took the cause directly to the public via the medium of television as a guest on the Gary Moore show, "I've Got a Secret," in January 1959. I used a single drop of adhesive to lift host Moore off the floor (see photo, right).

The cyanoacrylate adhesives were stronger glues than anything anyone had seen before. The first sale of superglue was to Mason and Hanger for an assembly job in an atomic bomb. In time, cyanoacrylate adhesives would revolutionize industries as different as auto makers, the manufacture of circuit boards, assembly of fine jewelry, and lightweight aircraft; they became an indispensable tool of woodworkers, model builders and curators of fossil museums. Considering that the average bond is one drop and that there are about 30,000 drops per pound, 1 million pounds will make some 30 billion individual bonds.

Sùperglue today is a booming $400 million-plus industry. Entire R&D departments at big manufacturers like Loctite, 3M and others are continually discovering or creating new superglue formulations, applications and markets.

Tissue Adhesives and More

Doctors had long dreamed of a tissue adhesive: a glue that could be used to mend flesh without the complications of sutures or other mechanical fasteners. All attempts to find a physiologically acceptable surgical adhesive had failed. I was the first to recognize and patent cyanoacrylates as adhesives for human tissues.

Because Eastman had no facilities for medical research in 1960, I entered into a cooperative agreement with Ethicon, a subsidiary of Johnson & Johnson, to investigate possible medical applications of the cyanoacrylates. A number of outstanding medical research groups, including Dr. DeBakey and his associates, participated in these investigations. This research went on for more than a decade.

Through experiments with laboratory animals and, later, in actual use on human subjects, the value of the cyanoacrylate medical adhesives was established.

The power of Superglue was demonstrated to the 1959 TV audience by using a single drop to lift discoverer Harry Coover (left) and "I've Got a Secret" host Gary Moore off of the floor during the popular CBS show. Photo is a frame from the original kinescope, courtesy of H. Coover.

Briefly, some of the medical problems for which the cyanoacrylates proved uniquely useful in these research studies were sutureless surgery, particularly rejoining veins, arteries or intestines. They were equally useful in sealing and reinforcing suture lines in more conventional procedures.

In ophthalmic surgery, these adhesives readily sealed small punctures or lesions in the eyeball—ordinarily very difficult to do—with sight-saving results. Corneal transplants were made safer and easier to perform. In cosmetic surgery, the use of cyanoacrylate to replace or supplement sutures greatly reduced scarring. Bleeding ulcers could be sealed with a coating of adhesive, which protected the ulcer from stomach acids while healing proceeded. This procedure could be accomplished through an endoscope without surgery. Repairs of soft organs, lung lesions and other serious damage could also be more easily done with these adhesives than by conventional methods.

Cyanoacrylate adhesives were particularly useful in sealing tooth sockets after extractions and in periodontal surgery. An unexpected bonus in periodontal surgery was that cyanoacrylate greatly reduced the postoperative pain suffered by the patient.

In all of these operations the adhesive made the work easier and quicker for the surgeon, reduced the stress on the patient, promoted rapid recovery of function or

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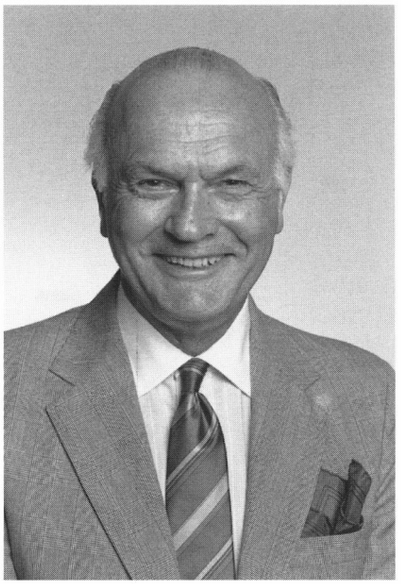
The Industrial Research Institute Achievement Award

Presented to HARRY W. COOVER

For his prolific scientific achievements recorded in more than 60 papers and 460 patents, and for the invention and innovation of cyanoacrylate adhesives.



Harry W. Coover, Executive Vice President and Chief Technical Officer (retired) of Eastman Chemical Company, has a rare combination of vision and practicality in recognizing potential solutions to market and production needs and opportunities. Prior to joining Eastman Chemical, he devised and patented a synthesis for Vitamin B-6. At Eastman, his scientific research covered an exceptionally broad range of subjects. He was one of the pioneers in the field of graft polymerization as a means of conferring new desirable characteristics to a preformed polymer without degrading the desirable properties of the host polymer. Based on this work, a graft copolymer composition was commercialized by Eastman as Verel modoacrylic fiber, as were several new Eastman plastics. Dr. Coover's pioneering research in organophosphorus chemistry resulted in the innovation of effective insecticides as well as flame-resistant polymers. His original work in organophosphorus chemistry led to an invitation as a visiting lecturer to the Polish Academy of Sciences in 1976.

Much of Dr. Coover's research was in the field of olefin polymerization, where his pioneering work included the discovery of the use of tricomponent catalysts, comprising a metal or organometallic compound, a transition metal halide, and an organic base, as a way of controlling the polymerization to yield highly stereoregular polymers. The first commercial process for making highly stereoregular polypropylene resulted directly from this work.

Dr. Coover may be best known today for the discovery and innovation of cyanoacrylate adhesives, commonly known as Superglue. He was the first to recognize and patent cyanoacrylates as adhesives for human tissues. Sutureless surgery, particularly rejoining veins, arteries, or intestines, was possible and was equally useful in sealing and reinforcing suture lines in more conventional procedures. In ophthalmic surgery, these adhesives readily sealed small punctures or lesions in the eyeball, ordinarily very difficult to do, with sight-saving results. Corneal transplants were made safer and easier to perform. In cosmetic surgery, the use of cyanoacrylate to replace or supplement sutures greatly reduced scarring. Bleeding ulcers could be sealed with a coating of adhesive, protecting the ulcer from stomach acids while healing. These adhesives were also useful in dental surgery to seal tooth sockets after extractions and in periodontal surgery. The most unusual and valuable use of the adhesives is as hemostatic agents. Uncontrollable bleeding, particularly in the repair of soft organs such as the liver or spleen, was instantly stopped by spraying a thin coating of cyanoacrylate on the bleeding surface.

Dr. Coover also received the IRI Medal in 1984 in recognition of his leadership of technological innovation, and the 1987 IRI Maurice Holland Award for the best paper published in 1986 in IRI's journal, *Research · Technology Management.*

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appearance, and sometimes made possible otherwise impossible repairs, thus saving lives.

Hemostatic Agents

Probably the most unusual and valuable use of the cyanoacrylates was as hemostatic agents, a use that departed somewhat from the original concept of a tissue-joining adhesive. Uncontrollable bleeding is a serious problem in surgery, particularly in the repair of soft organs such as the liver or spleen. It was found that a thin coating of cyanoacrylate sprayed on the bleeding surface almost instantly stopped the loss of blood. This was truly a life-saving procedure for it controlled bleeding when all other measures failed.

The ultimate test for cyanoacrylate medical adhesive came in the Vietnam War. Medical evacuation helicopters brought the seriously wounded to battle-zone surgical units, sometimes within minutes after injury. Once there, all too often even the most skilled surgeon could not save many of those suffering grave wounds of the chest or abdomen. Uncontrollable bleeding killed them before the damage could be repaired.

In 1966, a special surgical team trained and equipped with cyanoacrylate adhesive went to Vietnam and experienced almost miraculous results. A simple spray stopped the bleeding almost instantly, allowing time to treat the wounds by conventional means. Because of cyanoacrylate, many were saved who would otherwise have died. Several armies now include tubes of superglue variants in their first-aid kits.

Surgeons in tropical countries are using cyanoacrylates instead of stitches—the risks of infection are less. The 1985 Bradford Fair highlighted the advantages. A huge number of skin grafts were required in a very short time, and there were not enough people around who could stitch them into place.

Alan Roberts at the University of Hull and St. Luke's Hospital, Bradford, was on the emergency team. He decided to risk using commercial Superglue bought from local stores. The results were a delight—Roberts found that grafts that had been glued were much less scarring than those done with stitches. The adhesive broke down to harmless by-products at about the same rate as the wounds healed. There are numerous other stories recorded in the literature.

The Story Continues

Today, a number of prestigious research groups continue the investigation of cyanoacrylates as tissue adhesives and hemostatic agents for a wide range of surgical procedures. Cyanoacrylates are widely used by physicians in Canada, Europe and Japan for a number of surgical procedures.

Only recently, however, has the U.S. Food and Drug Administration begun to approve cyanoacrylates for surgical procedures in the United States.

We can expect the story of cyanoacrylates to continue well into the new millennium, as scientists and engineers in a broad range of disciplines continue their search for new and unique applications for cyanoacrylates. *Stay tuned.*

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Illustrations should be individually numbered, furnished one per page on 8-½ × 11-inch white paper, and be suitable for black-and-white reproduction, without redrawing.

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